Statistical Physics

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1 Classical Thermodynamics

1.1 Temperature and the Zeroth Law

1.1.1 Equilibrium

The zeroth law of thermodynamics: *Two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other.*

1.1.2 A Statistical Definition of Temperature

$$
\boxed{\begin{array}{c} E_1 \\ \Omega_1(E_1) \end{array}} \!\!-\!\! \boxed{\begin{array}{c} E_1 \\ \Omega_2(E_2) \end{array}}
$$
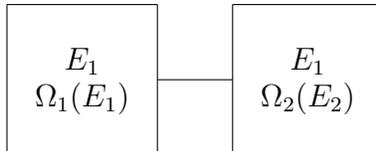
Two systems are only to exchange energy between themselves. *A system will appear to choose a macroscopic configuration that maximizes the number of microstates.* This idea is based on the following assumptions:

(1) Each one of the possible microstates of a system is equally likely to occur;

(2) The system's internal dynamics are such that the microstates of the system are continually changing;

(3) Given enough time, the system will explore all possible microstates and spend an equal time in each of them.

For our problem of two connected systems, the most probable di- vision of energy between the two systems is the one that maximizes $\Omega_1(E_1)\Omega_2(E_2)$, because this will correspond to the greatest number of possible microstates.

$$
\frac{\mathrm{d}}{\mathrm{d}E_1}\left[\Omega_1(E_1)\Omega_2(E_2)\right] = \Omega(E_2)\frac{\mathrm{d}\Omega(E_1)}{\mathrm{d}E_1} + \Omega(E_1)\frac{\mathrm{d}\Omega(E_2)}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}E_1} = \Omega_2\frac{\mathrm{d}\Omega_1}{\mathrm{d}E_1} - \Omega_1\frac{\mathrm{d}\Omega_2}{\mathrm{d}E_2} = 0 \quad (1.1)
$$

hence

$$
\frac{\mathrm{d}\ln\Omega_1}{\mathrm{d}E_1} = \frac{\mathrm{d}\ln\Omega_2}{\mathrm{d}E_2} \tag{1.2}
$$

We can define the **temperature** T by

$$
\frac{1}{k_BT} = \frac{\mathrm{d}\ln\Omega}{\mathrm{d}E} \tag{1.3}
$$

where k_B is the **Boltzmann constant**, which is given by

$$
k_B = 1.3807 \times 10^{-23} \ \mathrm{JK}^{-1} \tag{1.4}
$$

1.2 The First Law

1.2.1 Energy

The first law of thermodynamics: *Energy is conserved and heat and work are both forms of energy.*

$$dU = đQ + đW \tag{1.5}$$

The work can be expressed by

$$đW = -pdV \tag{1.6}$$

this equation is only true for a reversible change.

We now want to understand how adding heat can change the internal energy of gas. In general ,we can write $U = U(T,V)$. Hence

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{1.7}$$

We have that

$$đQ = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV \tag{1.8}$$

We can divide Eq.(1.8) by dT to obtain

$$\frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \frac{dV}{dT} \tag{1.9}$$

Hence the heat capacity at constant volume C_V is given by

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.10}$$

The heat capacity at constant pressure C_p is given by

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p \tag{1.11}$$

so that

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p \tag{1.12}$$

We define the **adiabatic index** γ by

$$\gamma = \frac{C_p}{C_V} \tag{1.13}$$

1.2.2 Isothermal and Adiabatic processes

Isothermal Expansion of an Ideal Gas

The word **isothermal** means "at constant temperature", and hence the isothermal process

$$\Delta T = 0 \tag{1.14}$$

For an ideal gas, we have $\mathrm{d}U = C_V \mathrm{d}T$, so that

$$\Delta U = 0 \tag{1.15}$$

hence

$$\mathrm{d}Q = -\text{đ}W = p\mathrm{d}V \tag{1.16}$$

the heat absorbed by the gas during an isothermal expansion from volume V_1 to volume V_2 of 1 mole of an ideal gas at temperature T is

$$\Delta Q = \int \text{đ}Q = \int_{V_1}^{V_2} p\mathrm{d}V = \int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V = nRT \ln \frac{V_2}{V_1} \tag{1.17}$$

Adiabatic Expansion of an Ideal Gas

The word **adiabatic** means "without flow of heat". We define a change to be **adiabatic** if it is both *adiathermal and reversible.* In an adiabatic expansion, therefore, there is no flow of heat and we have

$$\text{đ}Q = 0 \tag{1.18}$$

so that

$$\mathrm{d}U = \text{đ}W \tag{1.19}$$

For an ideal gas

$$C_V\mathrm{d}T = -p\mathrm{d}V = -\frac{nRT}{V}\mathrm{d}V \tag{1.20}$$

so that

$$\ln \frac{T_2}{T_1} = -\frac{R}{C_V} \ln \frac{V_2}{V_1} \tag{1.21}$$

For an ideal gas we have $C_p = C_V + R$, and dividing this by C_V

$$\gamma = \frac{C_p}{C_V} = 1 + \frac{R}{C_V} \tag{1.22}$$

so that Eq.(1.21) becomes

$$TV^{\gamma-1} = \text{constant} \tag{1.23}$$

or

$$p^{1-\gamma}T^{\gamma} = \text{constant} \tag{1.24}$$

and

$$pV^{\gamma} = \text{constant} \tag{1.25}$$

1.3   The Second Law

- **Clausius' statement pf the second law of thermodynamics**: No process is possible whose sole result is *the transfer of heat from a colder to a hotter body.*

- **Kelvin's statement pf the second law of thermodynamics**: No process is possible whose sole result is *the complete conversion of heat into work.*

Irreversible Change

$$\oint \frac{\text{đ}Q}{T} = \int_A^B \frac{\text{đ}Q}{T} - \int_A^B \frac{\text{đ}Q_{\text{rev}}}{T} \leq 0 \tag{1.26}$$

$$\int_A^B \frac{\text{đ}Q}{T} \leq \int_A^B \frac{\text{đ}Q_{\text{rev}}}{T} \tag{1.27}$$

$$\text{d}S = \int_A^B \frac{\text{đ}Q_{\text{rev}}}{T} \geq \int_A^B \frac{\text{đ}Q}{T} \tag{1.28}$$

Consider a thermally isolated system where $\text{đ}Q = 0$ for any process, so that

$$\text{d}S \geq 0 \tag{1.29}$$

The first law revisited

For a reversible process, we have

$$\text{đ}Q = T\text{d}S \tag{1.30}$$

Although the equation above only holds for a reversible process, we **always** have

$$\text{d}U = T\text{d}S - p\text{d}V \tag{1.31}$$

In fact, we can write

$$\text{d}U = \left(\frac{\partial U}{\partial S}\right)_V \text{d}S + \left(\frac{\partial U}{\partial V}\right)_S \text{d}V \tag{1.32}$$

so that

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad p = -\left(\frac{\partial U}{\partial V}\right)_S \tag{1.33}$$

hence

$$\frac{p}{T} = -\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_U \tag{1.34}$$

The Statistical Basis for Entropy

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \tag{1.35}$$

$$\frac{1}{k_B T} = \frac{\text{d}\ln\Omega}{\text{d}E} \tag{1.36}$$

$$S = k_B \ln\Omega \tag{1.37}$$

1.4 Thermodynamic Potentials

1.4.1 Maxwell's Relations

Till now, we have defined the following thermodynamic potentials

$$U \qquad F = U - TS \qquad H = U + pV \qquad G = U + pV - TS \tag{1.38}$$

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$$
\begin{array}{ccc}
U & \xrightarrow{\;+pV\;} & H \\
{\scriptstyle -TS}\Big\downarrow & & \Big\downarrow{\scriptstyle -TS} \\
F & \xrightarrow[\;+pV\;]{} & G
\end{array}
$$

- **Internal energy**

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N \tag{1.39}$$

- **Helmholtz free energy**

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N \tag{1.40}$$

- **Enthalpy**

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}N \tag{1.41}$$

- **Gibbs free energy**

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N \tag{1.42}$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \tag{1.43}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \tag{1.44}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{1.45}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{1.46}$$

Identify a Heat Capacity

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{1.47}$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{1.48}$$

Generalized Susceptibility

- Isobaric expansivity

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1.49}$$

- Adiabadic expansivity

$$\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \tag{1.50}$$

- Isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.51}$$

- Adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \tag{1.52}$$

Reciprocity Theorem

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} \tag{1.53}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{1.54}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \tag{1.55}$$

1.4.2   Availability

Availability A is defined by

$$A = U - T_0 S + p_0 V \tag{1.56}$$

and for any spontaneous change we have that $dA \leq 0$. This means that a system in contact with a reservoir will minimize A which means

- minimizing U when S and T are fixed.

- minimizing H when S and p are fixed.

- minimizing F when T and V are fixed.

- minimizing G when T and p are fixed.

1.5   The Third Law

$$\lim_{T \to 0} S(T) = 0 \tag{1.57}$$

2 The Fundamentals of Statistical Mechanics

2.1 The Fundamental Assumptions of Statistical Mechanics

A system will appear to choose a macroscopic configuration that maximizes the number of microstates. This idea is based on the following assumptions:

(1) Each one of the possible microstates of a system is equally likely to occur;

(2) The system's internal dynamics are such that the microstates of the system are continually changing;

(3) Given enough time, the system will explore all possible microstates and spend an equal time in each of them.

$$\text{Macrostate} \quad \Leftrightarrow \quad \text{Microstate}$$
$$\langle A(t) \rangle_{\text{ensemble}} = \sum_i P_i(t) A_i \tag{2.1}$$

2.2 Ensemble

- **The microcanonical ensemble**: an ensemble of systems that each have the same fixed energy.

- **The canonical ensemble**: an ensemble of systems, each of which can exchange its energy with a large reservoir of heat. This fixes the temperature T of the system.

- **The grand canonical ensumble**: an ensemble of systems, each of which can exchange both energy and particles with a large reservoir. This fixes the temperature T and the chemical potential μ of the system.

2.2.1 The Microcanonical Ensemble (N, V, E)

system
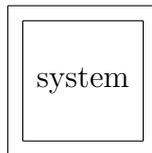
$$P_i = \frac{1}{\Omega} \tag{2.2}$$

The internal energy

$$U = \langle E \rangle = \sum_i P_i E_i = E \sum_i P_i = E \tag{2.3}$$

2.2.2 The Canonical Ensemble (N, V, T)

H.R.

sys
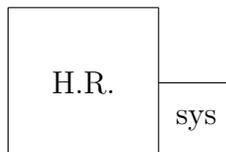
The Partition Function

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{Z} \tag{2.4}$$

where

$$Z = \sum_i e^{-\beta E_i} \tag{2.5}$$

- The internal energy

$$U = \langle E \rangle = \sum_i P_i E_i = -\frac{\partial \ln Z}{\partial \beta} \tag{2.6}$$

- Entropy

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i P_i \left(-\beta E_i - \ln Z \right) = \frac{1}{T} \left(U + k_B T \ln Z \right) \tag{2.7}$$

-

$$F = U - TS = -k_B T \ln Z \tag{2.8}$$

2.2.3 The Grand Canonical Ensemble (μ, V, T)
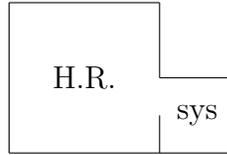
$$P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}} = \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} \tag{2.9}$$

where

$$\mathcal{Z} = \sum_i e^{-\beta(E_i - \mu N_i)} \tag{2.10}$$

- The number of particles

$$N = \sum_i P_i N_i = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} \tag{2.11}$$

- The internal energy

$$U = \sum_i P_i E_i = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu N \tag{2.12}$$

- Entropy

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i P_i \left(-\beta E_i + \beta \mu N_i - \ln \mathcal{Z} \right) = \frac{1}{T} \left(U - \mu N + k_B T \ln \mathcal{Z} \right) \tag{2.13}$$

The Chemical Potential

If you add a particle to a system, then the internal potential energy will change by an amount which we call the **chemical potential** μ.

$$dU = TdS - pdV + \mu dN \tag{2.14}$$

This means we can write an expression for μ

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{2.15}$$

With the definitions $F = U - TS$ and $G = U + pV - TS$, implies that

$$dF = -pdV - SdT + \mu dN \tag{2.16}$$

$$dG = Vdp - SdT + \mu dN \tag{2.17}$$

hence we can make the more useful definitions:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \qquad \text{or} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T} \tag{2.18}$$

Eq.(2.14) implies that

$$dS = \frac{dU}{T} + \frac{pdV}{T} - \frac{\mu dN}{T} \tag{2.19}$$

and with $S = S(U, V, N)$, we can write down

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \tag{2.20}$$

that we can therefore make the following identifications:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T} \tag{2.21}$$

Grand partition function

Consider a small system with fixed volume V and with energy ε and containing N particles, connected to a reservoir with energy $U - \varepsilon$ and $\mathcal{N} - N$ particles. We assume that $U \gg \varepsilon$ and $\mathcal{N} \gg N$. Using a Taylor expansion, we can write the entropy of the reservoir as

$$S(U - \varepsilon, \mathcal{N} - N) = S(U, \mathcal{N}) - \varepsilon\left(\frac{\partial S}{\partial U}\right)_{N,V} - N\left(\frac{\partial S}{\partial \mathcal{N}}\right)_{U,V} = S(U, \mathcal{N}) - \frac{1}{T}(\varepsilon - \mu N) \tag{2.22}$$

Using $S = k_B \ln \Omega$, we have

$$P \propto e^{S/k_B} \propto e^{\beta(\mu N - \varepsilon)} \tag{2.23}$$

Normalizing this distribution, we have

$$P_i = \frac{e^{-\beta(\mu N_i - E_i)}}{\mathcal{Z}} \tag{2.24}$$

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This is known as the **Gibbs distribution** and the situation is known as the **grand canonical ensemble**. The normalization constant is known as the **grand partition function** $\mathcal{Z}$

$$\mathcal{Z} = \sum_i e^{-\beta(\mu N_i - E_i)} \tag{2.25}$$

With the grand partition function $\mathcal{Z}$, we can write down the following equations

$$N = \sum_i N_i P_i = k_B T \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta \tag{2.26}$$

$$U = \sum_i E_i P_i = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu N \tag{2.27}$$

$$S = -k_B \sum_i P_i \ln P_i = \frac{1}{T}\left(U - \mu N + k_B T \ln \mathcal{Z}\right) \tag{2.28}$$

Grand Potential

The grand potential is defined by

$$\Phi_G = F - \mu N \tag{2.29}$$

Φ_G is a Legendre transform of F, from variable N to μ.

$$d\Phi_G = -S dT - p dV - N d\mu \tag{2.30}$$

$$\Phi_G = -k_B T \ln \mathcal{Z} \tag{2.31}$$

Extensive and Intensive Quantities

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \tag{2.32}$$

$F = U - TS$

$$F(T, \lambda V, \lambda N) = \lambda F(T, V, N) \tag{2.33}$$

$\Phi_G = F - \mu N$

$$\Phi_G(T, \lambda V, \mu) = \lambda \Phi_G(T, V, \mu) \tag{2.34}$$

$$\Phi_G(T, V, \mu) = -p(T, \mu)V \tag{2.35}$$

2.3 Equilibrium

$$dU = T dS - p dV + \mu dN \tag{2.36}$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \tag{2.37}$$

- **Thermal equilibrium**
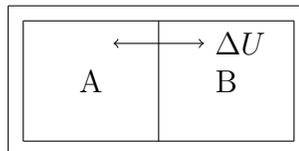
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \tag{2.38}$$

$$\frac{1}{k_B T} = \frac{\mathrm{d}\ln\Omega}{\mathrm{d}E} \tag{2.39}$$

- **Mechanical equilibrium**
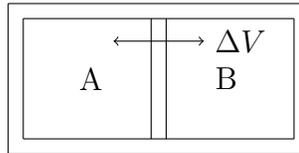
$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,U} \tag{2.40}$$

- **Chemical equilibrium**
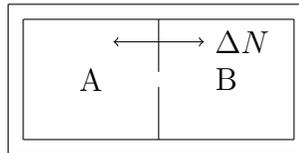
$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{2.41}$$

3 Classical Gases

3.1 Density of States

The ideal gas trapped in a box with sides of length L and volume $V = L^3$. If there are no interactions between particles, the energy eigenstates are simply plane waves,

$$\psi = \frac{1}{V} e^{i\vec{k}\cdot\vec{r}} \tag{3.1}$$

Boundary conditions require that the wavevector $\vec{k} = (k_1, k_2, k_3)$ is quantized as

$$k_i = \frac{2\pi n_i}{L} \qquad \text{with} \qquad n_i \in Z \tag{3.2}$$

the energy of the particle is

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2 \hbar^2}{2mL^2} \left(n_1^2 + n_2^2 + n_3^2 \right) \tag{3.3}$$

The quantum mechanical single particle partition function is given by the sum over all energy eigenstates,

$$Z_1 = \sum_n e^{-\beta E_n} \tag{3.4}$$

$$\sum_n \rightarrow \int \mathrm{d}^3 n = \frac{V}{(2\pi)^3} \int \mathrm{d}^3 k = \frac{4\pi V}{(2\pi)^3} \int_0^\infty k^2 \mathrm{d}k = \frac{V}{2\pi^2} \int_0^\infty k^2 \mathrm{d}k = \int g(k) \mathrm{d}k \tag{3.5}$$

where

$$g(k)\mathrm{d}k = \frac{V k^2 \mathrm{d}k}{2\pi^2} \tag{3.6}$$

3.2 Ideal Gas

$$Z_1 = \int_0^\infty e^{-\beta E(k)} g(k) \mathrm{d}k \tag{3.7}$$

The energy of a single molecule with wave vector k is given by

$$E(k) = \frac{\hbar^2 k^2}{2m} \tag{3.8}$$

Hence

$$Z_1 = \int_0^\infty \exp\left(-\beta \frac{\hbar^2 k^2}{2m} \right) \frac{V k^2 \mathrm{d}k}{2\pi^2} = \frac{V}{\hbar^3} \left(\frac{mk_B T}{2\pi} \right)^{\frac{3}{2}} \tag{3.9}$$

which can be writen as

$$Z_1 = V n_Q \qquad \text{where} \qquad n_Q = \frac{1}{\hbar^3} \left(\frac{mk_B T}{2\pi} \right)^{\frac{3}{2}} \tag{3.10}$$

where n_Q is known as the **quantum concentration**. We can define λ_{th}, the **thermal wavelength**, as follows:

$$\lambda_{\text{th}} = n_Q^{-\frac{1}{3}} = \hbar\sqrt{\frac{2\pi}{mk_B T}} = \frac{h}{\sqrt{2\pi mk_B T}} \tag{3.11}$$

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and hence we can also write

$$Z_1 = \frac{V}{\lambda_{\text{th}}^3} \tag{3.12}$$

- If the N particles are distinguishable

$$Z_N = (Z_1)^N \tag{3.13}$$

- If the N particles are indistinguishable

$$Z_N = \frac{(Z_1)^N}{N!} \tag{3.14}$$

$$F = -k_B T \ln Z_N = -k_B T N \ln V - k_B \frac{3N}{2} T \ln T - k_B T \times \text{constant} \tag{3.15}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N k_B T}{V} = n k_B T \tag{3.16}$$

3.3 Interacting Gas

The total innternal energy U of the molecules in a gas can be written as

$$U = U_{\text{K.E.}} + U_{\text{P.E.}} \tag{3.17}$$

And the partition function is given by

$$Z = Z_{\text{K.E.}} Z_{\text{P.E.}} = \frac{Z_1^N}{N!} Z_{\text{P.E.}} \tag{3.18}$$

$$Z_{\text{P.E.}} = \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N e^{-\beta \sum_{i<j} U(r_{ij})} \tag{3.19}$$

The obvious way thing to try is to Taylor expand

$$e^{-\beta \sum_{i<j} U(r_{ij})} = 1 - \beta \sum_{i<j} U(r_{ij}) + \frac{\beta^2}{2} \sum_{i<j,k<l} U(r_{ij})U(r_{kl}) + \cdots \tag{3.20}$$

Unfortunately, this isn't so useful. We want each term to be smaller than the preceding one. But as $r_{ij} \to 0$, $U(r_{ij}) \to \infty$, which doesn't look promising for an expansion parameter.

Instead of proceeding with Taylor expansion, we will instead choose to work with **Mayer function**

$$f(r) = e^{-\beta U(r)} - 1 \tag{3.21}$$

This is a nicer expansion parameter. When $r \to \infty$, $f(r) \to 0$; when $r \to 0$, $f(r) \to -1$. So we can write down

$$Z_{\text{P.E.}} = \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N \prod_{i<j} (1 + f_{ij})$$

$$= \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N \left(1 + \sum_{i<j} f_{ij} + \sum_{i<j,k<l} f_{ij} f_{kl} + \cdots \right) \tag{3.22}$$

We assume that **only one pair of molecules are close at one time**. The number of ways to select a pair of molecules from N molecules is

$$C_N^2 = \frac{N(N-1)}{2} \approx \frac{N^2}{2} \quad (N \to \infty) \tag{3.23}$$

hence

$$
\begin{aligned}
Z_{\text{P.E.}} &\approx \frac{1}{V^N} \int \cdots \int d^3r_1 \cdots d^3r_N \left(1 + \sum_{i<j} f_{ij} \right) \\
&= 1 + \frac{1}{V^N} \int \cdots \int d^3r_1 \cdots d^3r_N \left(\sum_{i<j} f_{ij} \right) \\
&\approx 1 + \frac{N^2}{2V^N} \int \cdots \int d^3r_1 \cdots d^3r_N \left[e^{-\beta U(r)} - 1 \right] \\
&= 1 + \frac{N^2}{2V} \int d^3r \left[e^{-\beta U(r)} - 1 \right]
\end{aligned}
\tag{3.24}
$$

and writing $B(T)$ (the virial coefficient) as

$$B(T) = \frac{N}{2} \int d^3r \left[1 - e^{-\beta U(r)} \right] \tag{3.25}$$

we have that

$$Z_{\text{P.E.}} \approx 1 - \frac{NB(T)}{V} \tag{3.26}$$

$$Z = Z_{K.E.} Z_{P.E.} = \frac{Z_1^N}{N!} \left[1 - \frac{NB(T)}{V} \right] \tag{3.27}$$

and hence

$$F = -k_B T \ln Z = -k_B T \ln \left[Z_{K.E.} \left(1 - \frac{NB(T)}{V} \right) \right] \approx F_0 + \frac{Nk_B T B(T)}{V} \tag{3.28}$$

the pressure

$$p = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{Nk_B T}{V} + \frac{Nk_B T B(T)}{V^2} \tag{3.29}$$

Reranging, we have that for one mole of gas

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} \tag{3.30}$$

3.3.1 The van der Waals Gas

The most commonly used model of real gas behaviour is the **van der Waals gas**.

- Intermolecular interactions
- The non-zero size of molecules

The equation of state for a van der Waals gas is

$$\left(p + \frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}} - b) = RT \tag{3.31}$$
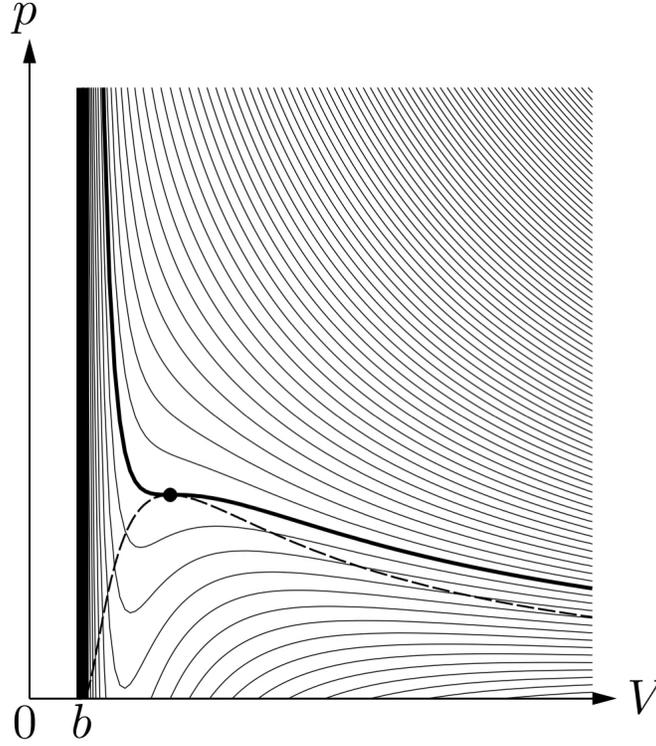
Multiplying Eq.(3.31) by V^2 for one mole of van der Waals gas (where $V_{\mathrm{m}} = V$), we have

$$pV^3 - (pb + RT)V^2 + aV - ab = 0 \tag{3.32}$$

The equation of state for one mole of van der Waals gas can be written with p as the subject as follows:

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \tag{3.33}$$

The Helmholtz function F is related to p by $p = -(\partial F/\partial V)_T$ and so

$$F = f(T) - RT\ln(V - b) - \frac{a}{V} \tag{3.34}$$

hence the Gibbs function is

$$G = F + pV = f(T) - RT\ln(V - b) - \frac{a}{V} + pV \tag{3.35}$$
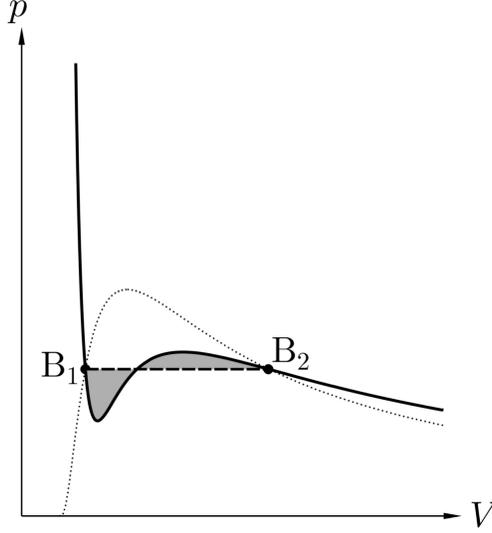
Figure 1: The Maxwell construction for the van der Waals gas. Phase coex- istence occurs between points B_1 and B_2 when the shaded areas are equal. The dotted line shows the locus of such points for different temperatures

$$G(p_{B_2}, T) = G(p_{B_1}, T) + \int_{p_{B_1}}^{p_{B_2}} \left(\frac{\partial G}{\partial p} \right)_T dp = G(p_{B_1}, T) + \int_{B_1}^{B_2} V dp \tag{3.36}$$

and since $G(p_{B_2}, T) = G(p_{B_1}, T)$, we have that

$$\int_{B_1}^{B_2} V dp = 0 \tag{3.37}$$

Find the temperature T_c, pressure p_c, and volume V_c at the critical point of a van der Waals gas

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \tag{3.38}$$

$$\left(\frac{\partial p}{\partial V} \right)_{T_c} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V^3} = 0 \tag{3.39}$$

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_{T_c} = \frac{2k_B T_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \tag{3.40}$$

so the **critical volume** V_c, the **critical temperature** T_c and the **critical pressure** p_c are given by

$$V_c = 3b \qquad\qquad T_c = \frac{8a}{27Rb} \qquad\qquad p_c = \frac{a}{27b^2} \tag{3.41}$$

We then have

$$\frac{p_c V_c}{RT_c} = \frac{3}{8} \tag{3.42}$$

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3.3.2 The Law of Corresponding States

We define the **reduced** variables,

$$\bar{T} = \frac{T}{T_c} \qquad\qquad \bar{V} = \frac{V}{V_c} \qquad\qquad \bar{p} = \frac{p}{p_c} \tag{3.43}$$

Substituting the reduced coordinates into Eq.(3.38) we find that

$$p_c \bar{p} = \frac{RT_c \bar{T}}{V_c \bar{V} - b} - \frac{a}{V_c^2 \bar{V}^2} \tag{3.44}$$

and this can be rearranged to give

$$\bar{p} = \frac{8\bar{T}}{3\bar{V} - 1} - \frac{3}{\bar{V}^2} \tag{3.45}$$

3.3.3 The Dieterici Equation

$$p = p_{\text{repulsive}} + p_{\text{attractive}} \tag{3.46}$$

$$p_{\text{repulsive}} = \frac{RT}{V - b} \tag{3.47}$$

$$p_{\text{attractive}} = -\frac{a}{V^2} \tag{3.48}$$

3.3.4 Virial Expansion

$$U = U_{\text{K.E.}} + U_{\text{P.E.}} \tag{3.49}$$

$$Z = Z_{\text{K.E.}} Z_{\text{P.E.}} \tag{3.50}$$

$$
\begin{aligned}
Z_{\text{P.E.}} &= \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N e^{-\beta U_{\text{P.E.}}} \\
&= \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N e^{-\frac{1}{2}\beta \sum_{i \neq j} V(|\vec{r}_i - \vec{r}_j|)} \\
&= 1 + \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N \left[e^{-\frac{1}{2}\beta \sum_{i \neq j} V(|\vec{r}_i - \vec{r}_j|)} - 1 \right] \\
&\approx 1 + \frac{N^2}{2V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N \left[e^{-\beta V(r)} - 1 \right] \\
&= 1 + \frac{N^2}{2V} \int d^3 r \left[e^{-\beta V(r)} - 1 \right]
\end{aligned} \tag{3.51}
$$

$$B(T) = \frac{N}{2} \int d^3 r \left[1 - e^{-\beta V(r)} \right] \tag{3.52}$$

$$Z_{\text{P.E.}} \approx 1 - \frac{NB(T)}{V} \approx \exp\left[-\frac{NB(T)}{V} \right] \tag{3.53}$$

$$F = -k_B T \ln Z = -k_B T \ln(Z_{\text{K.E.}} Z_{\text{P.E.}}) = F_0 - k_B T \ln Z_{\text{P.E.}} = F_0 + \frac{N k_B T B(T)}{V} \tag{3.54}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} + \frac{Nk_BTB(T)}{V^2} \tag{3.55}$$

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} \tag{3.56}$$

3.4 Cooling Real Gas

3.4.1 The Joule Expansion

Joule coefficient μ_{J}

$$u_{\mathrm{J}} = \left(\frac{\partial T}{\partial V}\right)_U \tag{3.57}$$

3.4.2 Isothermal Expansion

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{3.58}$$

$$\Delta U = \int_{V_1}^{V_2} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V \tag{3.59}$$

4 Quantum Gases

4.1 Photons

In the language of quantum mechanics, electromagnetic waves can be quantized as a set of particles, which are known as **photons**. Each photon has energy

$$E = \hbar\omega \tag{4.1}$$

the density of states of electromagnetic waves as a function of wave vector k is given by

$$g(k)\mathrm{d}k = \frac{Vk^2\mathrm{d}k}{2\pi^2} \times 2 = \frac{Vk^2\mathrm{d}k}{\pi^2} \tag{4.2}$$

where the factor 2 corresponds to the two possible polarizations of the electromagnetic waves. According to $\omega = ck$, the density of states of angular frequency ω is given by

$$g(\omega) = g(k)\frac{\mathrm{d}k}{\mathrm{d}\omega} = \frac{g(k)}{c} \tag{4.3}$$

and hence

$$g(\omega)\mathrm{d}\omega = \frac{V\omega^2\mathrm{d}\omega}{\pi^2c^3} \tag{4.4}$$

A state with N such photons has energy $E = N\hbar\omega$. Summing over all N gives us the partition function for photons at fixed frequency,

$$Z_\omega = 1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots = \frac{1}{1 - e^{-\beta\hbar\omega}} \tag{4.5}$$

So we have

$$\ln Z = \int g(\omega)\ln Z_\omega \mathrm{d}\omega = -\frac{V}{\pi^2c^3}\int_0^\infty \omega^2\ln\left(1 - e^{-\beta\hbar\omega}\right)\mathrm{d}\omega \tag{4.6}$$

The internal energy U for the photon gas is given by

$$U = -\frac{\partial\ln Z}{\partial\beta} = \frac{V\hbar}{\pi^2c^3}\int_0^\infty \frac{\omega^3\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1} = \frac{V\pi^2k_B^4}{15c^3\hbar^3}T^4 \tag{4.7}$$

the energy density

$$u = \frac{U}{V} = \frac{\pi^2k_B^4}{15c^3\hbar^3}T^4 = AT^4 \tag{4.8}$$

where

$$A = \frac{\pi^2k_B^4}{15c^3\hbar^3} \tag{4.9}$$

We know that $A = 4\sigma/c$ and the Stefan-Boltzmann constant σ is

$$\sigma = \frac{\pi^2k_B^4}{60c^2\hbar^3} = 5.67 \times 10^{-8} \text{ W m}^{-2}\text{K}^{-4} \tag{4.10}$$

4.1.1 Black-body Distribution

The expression in Eq.(4.8) can be written as

$$u = \frac{U}{V} = \int u_\omega \mathrm{d}\omega \tag{4.11}$$

so the spectral energy density is given by

$$u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{4.12}$$

This is the **Planck distribution** or **black-body distribution**. Similarly, with the relation $\omega = 2\pi\nu$ and $\nu = c/\lambda$, we have

$$u_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\beta h\nu} - 1} \tag{4.13}$$

$$u_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\beta hc/\lambda} - 1} \tag{4.14}$$

We can easily determine where this maximum occurs by finding the solution to $\mathrm{d}u_\omega/\mathrm{d}\omega = 0$. It is

$$\omega_{\mathrm{max}} = \xi\frac{k_B T}{\hbar} \qquad \text{where} \qquad \xi \approx 2.822 \tag{4.15}$$

and the wavelength

$$\lambda_{\mathrm{max}} \approx 10 \ \mu\mathrm{m} \tag{4.16}$$

4.1.2 The Einstein A and B coefficients

4.2 Phonons

4.2.1 The Einstein Model

The **Einstein model** treats the problem by making the assumption that **all vibrational modes of the solid have the same frequency** ω_E. There are $3N$ such modes. We will assume that these normal modes are independent and do not interact with each other. In this case, the partition function Z can be written as the product

$$Z = \prod_{k=1}^{3N} Z_k \tag{4.17}$$

$$\ln Z = \prod_{k=1}^{3N} \ln Z_k \tag{4.18}$$

where Z_k is the partition function of a single mode

$$Z_k = \sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)\hbar\omega_E\beta} = \frac{e^{-\frac{1}{2}\hbar\omega_E\beta}}{1 - e^{-\hbar\omega_E\beta}} \tag{4.19}$$

This expression is independent of k so the partion function is $Z = (Z_k)^{3N}$ and hence

$$\ln Z = 3N \ln Z_k = 3N \left[-\frac{1}{2}\hbar\omega_E\beta - \ln\left(1 - e^{-\hbar\omega_E\beta}\right) \right] \tag{4.20}$$

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and the internal energy U is

$$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right) = \frac{3N}{2}\hbar\omega_E + \frac{3N}{1 - e^{-\hbar\omega\beta}}\hbar\omega_E e^{-\hbar\omega_E\beta}$$

$$= \frac{3N}{2}\hbar\omega_E + \frac{3N\hbar\omega_E}{e^{\hbar\omega\beta} - 1} \tag{4.21}$$

Define Einstein temperature Θ_E by writing $\hbar\omega_E = k_B\Theta_E$, hence

$$\Theta_E = \frac{\hbar\omega_E}{k_B} \tag{4.22}$$

So the molar internal energy can be written as

$$U = 3R\Theta_E\left[\frac{1}{2} + \frac{1}{\exp\left(\frac{\Theta_E}{T}\right) - 1}\right] \tag{4.23}$$

In the high-temperature limit, $U \to 3RT$.

The molar heat capacity of an Einstein solid is given by

$$C = \left(\frac{\partial U}{\partial T}\right) = 3R\frac{x^2 e^x}{(e^x - 1)^2} \qquad \text{where} \qquad x = \frac{\Theta_E}{T} \tag{4.24}$$

- As $T \to 0$, $x \to \infty$ and $C \to 3Rx^2 e^{-x}$.

- As $T \to \infty$, $x \to 0$ and $C \to 3R$.

The high temperature result is known as the **Dulong-Petit rule**.

4.2.2 The Debye Model

Different from the Einstein model, the Debye model assumes a distribution of frequencies. The number of vibrational states with frequencies between ω and $\omega + \mathrm{d}\omega$ should be given by $g(\omega)\mathrm{d}\omega$ and we require that the total number of normal modes be given by

$$\int g(\omega)\mathrm{d}\omega = 3N \tag{4.25}$$

The density of states of lattice vibrations in 3-D as a function of q is given by

$$g(q)\mathrm{d}q = \frac{4\pi q^2 \mathrm{d}q}{(2\pi/L)^3} \times 3 = \frac{3V q^2 \mathrm{d}q}{2\pi^2} \tag{4.26}$$

where $V = L^3$ and the factor 3 corresponds to the three possible "polarizations" of the lattice vibration. We assume that

$$\omega = v_s q \tag{4.27}$$

and hence

$$g(\omega)\mathrm{d}\omega = \frac{3V\omega^2\mathrm{d}\omega}{2\pi^2 v_s^3} \tag{4.28}$$

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Debye frequency ω_D defined by

$$\int_0^{\omega_D} g(\omega)\mathrm{d}\omega = 3N \tag{4.29}$$

implied that

$$\omega_D = \left(\frac{6N\pi^2 v_s^3}{V}\right)^{\frac{1}{3}} \tag{4.30}$$

This allows us to rewrite Eq.(4.28) as

$$g(\omega)\mathrm{d}\omega = \frac{9N\omega^2\mathrm{d}\omega}{\omega_D^3} \tag{4.31}$$

we define the **Debye temperature** Θ_D by

$$\Theta_D = \frac{\hbar\omega_D}{k_B} \tag{4.32}$$

The partition function for phonons of a fixed frequency ω

$$Z_\omega = \sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)\hbar\omega\beta} = \frac{e^{-\frac{1}{2}\hbar\omega\beta}}{1-e^{-\hbar\omega\beta}} \tag{4.33}$$

Summing over all frequencies, the partition function is then

$$\ln Z = \int_0^{\omega_D} g(\omega)\ln Z_\omega \mathrm{d}\omega = \int_0^{\omega_D} g(\omega)\ln\left(\frac{e^{-\frac{1}{2}\hbar\omega_E\beta}}{1-e^{-\hbar\omega_E\beta}}\right)\mathrm{d}\omega = -\frac{9}{8}N\hbar\omega_D\beta - \frac{9}{\omega_D^3}\int_0^{\omega_D}\omega^2\ln\left(1-e^{-\hbar\omega\beta}\right)\mathrm{d}\omega \tag{4.34}$$

The internal energy U

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3\mathrm{d}\omega}{e^{\hbar\omega\beta}-1} \tag{4.35}$$

The heat capacity C

$$C = \frac{\partial U}{\partial T} = \frac{9N\hbar}{\omega_D}\int_0^{\omega_D}\frac{-\omega^3\mathrm{d}\omega}{(e^{\hbar\omega\beta}-1)^2}e^{\hbar\omega\beta}\left(-\frac{\hbar\omega}{k_BT^2}\right) \tag{4.36}$$

Making the substition $x = \hbar\beta\omega$ and $x_D = \hbar\beta\omega_D$, the molar heat capacity implies

$$C = \frac{9R}{x_D^3}\int_0^{x_D}\frac{x^4 e^x \mathrm{d}x}{(e^x-1)^2} \tag{4.37}$$

- As $T \to 0$, $x \to \infty$

$$C \to \frac{9R}{x_D^3}\int_0^{\infty}\frac{x^4 e^x \mathrm{d}x}{(e^x-1)^2} = \frac{12R\pi^4}{5x_D^3} = \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_D}\right)^3 \tag{4.38}$$

- As $T \to \infty$, $x \to 0$, $e^x - 1 \to x$

$$C \to \frac{9R}{x_D^3}\int_0^{x_D}x^2\mathrm{d}x = 3R \tag{4.39}$$

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4.3 Bosons

$$\psi(\vec{r}_2, \vec{r}_1) = \psi(\vec{r}_1, \vec{r}_2) \tag{4.40}$$

4.3.1 Bose-Einstein Distribution

Let's denote the number of particles in state $|r\rangle$ as n_r. The grand partition function for the state is

$$\mathcal{Z}_r = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = \frac{1}{1 - e^{-\beta(E_r - \mu)}} \tag{4.41}$$

We assumed that the sum above converges, which is true only if $(E_r - \mu) > 0$. We will set the ground state to have energy $E_0 = 0$, so we should have $\mu < 0$.

$$\mathcal{Z} = \prod_r \mathcal{Z}_r = \prod_r \frac{1}{1 - e^{-\beta(E_r - \mu)}} \tag{4.42}$$

$$\ln \mathcal{Z} = \sum_r \ln \mathcal{Z}_r = -\sum_r \ln \left[1 - e^{-\beta(E_r - \mu)} \right] \tag{4.43}$$

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \sum_r \frac{e^{-\beta(E_r - \mu)}}{1 - e^{-\beta(E_r - \mu)}} = \sum_r \frac{1}{e^{\beta(E_r - \mu)} - 1} = \sum_r \langle n_r \rangle \tag{4.44}$$

Here $\langle n_r \rangle$ denotes the average number of particles in the state $|r\rangle$,

$$\langle n_r \rangle = \frac{1}{e^{\beta(E_r - \mu)} - 1} \tag{4.45}$$

This is the **Bose-Einstein distribution**.

$$f(E) = \frac{1}{e^{\beta(E - \mu)} - 1} \tag{4.46}$$

4.3.2 Ideal Bose Gas

$$E = \frac{\hbar^2 k^2}{2m} \tag{4.47}$$

$$g(E) = (2s + 1) \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} \tag{4.48}$$

We use the notation of fugacity, $z = e^{\beta\mu}$. The particle number is

$$N = \int \mathrm{d}E \frac{g(E)}{z^{-1} e^{\beta E} - 1} = (2s + 1) \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}} \mathrm{d}E}{z^{-1} e^{\beta E} - 1} \tag{4.49}$$

The average energy is

$$U = \int \mathrm{d}E \frac{E g(E)}{z^{-1} e^{\beta E} - 1} = (2s + 1) \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{3}{2}} \mathrm{d}E}{z^{-1} e^{\beta E} - 1} \tag{4.50}$$

And the grand potential

$$\Phi_G = -pV = -k_B T \ln \mathcal{Z} = \frac{1}{\beta} \int_0^\infty \mathrm{d}E g(E) \ln \left(1 - z e^{-\beta E} \right) = -\frac{2}{3} U \tag{4.51}$$

4.3.3 Bose-Einstein Condensation (BEC)

At zero temperature, all the atoms will be in the lowest-energy available state, and since bosons are allowed in any given state, which means that every atom will be in the ground state. For atoms confined to a box of volume $V = a^3$, the energy of the ground state is

$$E_0 = \frac{h^2}{8ma^2}\left(1^2 + 1^2 + 1^2\right) = \frac{3h^2}{8ma^2} \tag{4.52}$$

The avarage number of atoms in the ground state is given by Bose-Einstein distribution

$$N_0 = \frac{1}{e^{\beta(E_0 - \mu)} - 1} \tag{4.53}$$

When $T \to 0$, Taylor expansion gives

$$N_0 = \frac{1}{1 + \beta(E_0 - \mu) - 1} = \frac{1}{\beta(E_0 - \mu)} \qquad (N_0 \gg 1) \tag{4.54}$$

The chemical potential μ, therefore, must be equal to E_O at $T = 0$, and just a tiny bit less than E_O when T is nonzero but still sufficiently small that nearly all of the atoms are in the ground state. The remaining question is this: *How low must the temperature be, in order for N_0 to be large?*

The total number N of bosons, which is

$$N = (2s+1)\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{E^{\frac{1}{2}}\mathrm{d}E}{z^{-1}e^{\beta E} - 1} = (2s+1)\frac{V}{4\pi^2}\left(\frac{2mk_BT_c}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{x^{\frac{1}{2}}\mathrm{d}x}{e^x - 1} \propto T_c^{\frac{3}{2}} \tag{4.55}$$

$$N_{\text{excited}} = (2s+1)\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{E^{\frac{1}{2}}\mathrm{d}E}{z^{-1}e^{\beta E} - 1} \approx (2s+1)\frac{V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{x^{\frac{1}{2}}\mathrm{d}x}{e^x - 1} \propto T^{\frac{3}{2}} \tag{4.56}$$

$$N_0 = N - N_{\text{excited}} = \left[1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}\right]N \tag{4.57}$$

The abrupt accumulation of atoms in the ground state at temperatures below T_c is called **Bose-Einstein condensation**.

4.4 Fermions

4.4.1 Fermi-Dirac Distribution

$$\psi(\vec{r}_2, \vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_2) \tag{4.58}$$

Pauli exclusion principle shows that fermions cannot sit in the same state, each state can either be empty or singly occupied, so that $\{n_r\} = \{0, 1\}$, and hence the grand partition function

$$\mathcal{Z}_r = \sum_{n_r=0,1} e^{-\beta n_r(E_r - \mu)} = 1 + e^{-\beta(E_r - \mu)} \tag{4.59}$$

$$\mathcal{Z} = \prod_r \mathcal{Z}_r = \prod_r \left[1 + e^{-\beta(E_r - \mu)}\right] \tag{4.60}$$

$$\ln \mathcal{Z} = \sum_r \ln \mathcal{Z}_r = \sum_r \ln \left[1 + e^{-\beta(E_r - \mu)} \right] \tag{4.61}$$

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \sum_r \frac{e^{-\beta(E_r - \mu)}}{1 + e^{-\beta(E_r - \mu)}} = \sum_r \frac{1}{e^{\beta(E_r - \mu)} + 1} = \sum_r \langle n_r \rangle \tag{4.62}$$

the average number of particles in the state $|r\rangle$ is

$$\langle n_r \rangle = \frac{1}{e^{\beta(E_r - \mu)} + 1} \tag{4.63}$$

This is the **Fermi-Dirac distribution**.

$$f(E) = \frac{1}{e^{\beta(E - \mu)} + 1} \tag{4.64}$$

4.4.2 Ideal Fermi Gas

We'll look again at non-interacting, non-relativistic particles with $E = \hbar^2 k^2 / 2m$. Since fermions necessarily have $\frac{1}{2}$-integer spin, s, there is always a degeneracy factor when counting the number of states given by

$$g_s = 2s + 1 \tag{4.65}$$

For non-relativistic fermions, the density of states is

$$g(E) = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} \tag{4.66}$$

We use the notation of fugacity, $z = e^{\beta \mu}$. The particle number is

$$N = \int dE \frac{g(E)}{z^{-1} e^{\beta E} + 1} = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}} dE}{z^{-1} e^{\beta E} + 1} \tag{4.67}$$

The average energy is

$$U = \int dE \frac{E g(E)}{z^{-1} e^{\beta E} + 1} = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{3}{2}} dE}{z^{-1} e^{\beta E} + 1} \tag{4.68}$$

And the grand potential

$$\Phi_G = -pV = -k_B T \ln \mathcal{Z} = -\frac{1}{\beta} \int dE g(E) \ln \left(1 + z e^{-\beta E} \right) = -\frac{2}{3} U \tag{4.69}$$

4.4.3 Degenerate Fermi Gas and the Fermi Surface

In the extreme limit $T \to 0$, the Fermi-Dirac distribution becomes very simple: a state is either filled or empty.

$$\frac{1}{e^{\beta(E_r - \mu)} + 1} \quad \to \quad \begin{cases} 1 & \text{for } E < \mu \\ 0 & \text{for } E > \mu \end{cases} \tag{4.70}$$

Each fermion that we throw into the system settles into the lowest available energy state. These are successively filled until we run out of particles. The energy of the last filled state is

called the Fermi energy and is denoted as E_F. Mathematically, it is the value of the chemical potential at $T = 0$,

$$\mu(T = 0) = E_F = \frac{\hbar^2 k_F^2}{2m} \tag{4.71}$$

The particle number

$$N = \int_0^{E_F} g(E)\mathrm{d}E = \frac{g_s V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_F^{\frac{3}{2}} \tag{4.72}$$

The average energy

$$U = \int_0^{E_F} Eg(E)\mathrm{d}E = \frac{3}{5} N E_F \tag{4.73}$$

And the pressure of the degenerate Fermi gas

$$pV = \frac{2}{3} U = \frac{2}{5} N E_F \tag{4.74}$$

Even at zero temperature, the gas has non-zero pressure, known as degeneracy pressure. It is a consequence of the Pauli exclusion principle.

4.4.4 The Fermi Gas at Low Temperature

4.4.5 A More Rigorous Approach: The Sommerfeld Expansion

Example: Evaluate the integral

$$I = \int_0^\infty \phi(E)f(E)\mathrm{d}E \tag{4.75}$$

as a power series in temperature. Where

$$f(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \tag{4.76}$$

Solution: Consider the function

$$\psi(E) = \int_0^E \phi(E')\mathrm{d}E' \tag{4.77}$$

which is defined so that

$$\phi(E) = \frac{\mathrm{d}\psi}{\mathrm{d}E} \tag{4.78}$$

and therefore

$$I = \int_0^\infty \frac{\mathrm{d}\psi}{\mathrm{d}E} f(E)\mathrm{d}E = f(E)\psi(E)\Big|_0^\infty - \int_0^\infty \psi(E)\frac{\mathrm{d}f}{\mathrm{d}E}\mathrm{d}E = -\int_0^\infty \psi(E)\frac{\mathrm{d}f}{\mathrm{d}E}\mathrm{d}E \tag{4.79}$$

Let $x = \beta(E - \mu)$ and hence

$$\frac{\mathrm{d}f}{\mathrm{d}E} = -\frac{\beta e^x}{(e^x + 1)^2} \tag{4.80}$$

Writing $\psi(E)$ as a power series in x as

$$\psi(E) = \sum_{s=0}^\infty \frac{x^s}{s!} \left(\frac{\mathrm{d}^s\psi}{\mathrm{d}x^s}\right)_{x=0} \tag{4.81}$$

We can express I as a power series of integrals as follows:

$$I = \sum_{s=0}^{\infty} \frac{1}{s!} \left(\frac{\mathrm{d}^s \psi}{\mathrm{d}x^s} \right)_{x=0} \int_{-\beta\mu}^{\infty} \frac{x^s e^x \mathrm{d}x}{(e^x + 1)^2} \tag{4.82}$$

When $\beta\mu \gg 1$, we can replace the lower limit with $-\infty$. The integral vanished for odd s, but for even s we have

$$
\begin{aligned}
\int_{-\infty}^{\infty} \frac{x^s e^x \mathrm{d}x}{(e^x + 1)^2} &= 2 \int_{0}^{\infty} \frac{x^s e^x \mathrm{d}x}{(e^x + 1)^2} = 2 \int_{0}^{\infty} \frac{x^s e^{-x} \mathrm{d}x}{(e^{-x} + 1)^2} \\
&= 2 \int_{0}^{\infty} \mathrm{d}x\, x^s e^{-x} \sum_{n=0}^{\infty} (-1)^n (n+1) e^{-nx} \\
&= 2 \sum_{n=0}^{\infty} (-1)^n (n+1) \int_{0}^{\infty} \mathrm{d}x\, x^s e^{-(n+1)x} \\
&= 2 \sum_{n=1}^{\infty} (-1)^{n+1} n \int_{0}^{\infty} x^s e^{-nx} \mathrm{d}x \\
&= 2(s!) \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^s} = 2(s!) \left(1 - 2^{1-s} \right) \zeta(s)
\end{aligned}
\tag{4.83}
$$

where $\zeta(s)$ is the Riemann ζ function. Thus the integral is

$$
\begin{aligned}
I &= 2 \sum_{s=0,2,4,\cdots}^{\infty} \left(\frac{\mathrm{d}^s \psi}{\mathrm{d}x^s} \right)_{x=0} \left(1 - 2^{1-s} \right) \zeta(s) \\
&= \psi(x=0) + \frac{\pi^2}{6} \left(\frac{\mathrm{d}^2 \psi}{\mathrm{d}x^2} \right)_{x=0} + \frac{7\pi^4}{360} \left(\frac{\mathrm{d}^4 \psi}{\mathrm{d}x^4} \right)_{x=0} + \cdots \\
&= \int_{0}^{\mu} \phi(E) \mathrm{d}E + \frac{\pi^2}{6} (k_B T)^2 \left(\frac{\mathrm{d}\phi}{\mathrm{d}E} \right)_{E=\mu} + \frac{7\pi^4}{360} (k_B T)^4 \left(\frac{\mathrm{d}^3 \phi}{\mathrm{d}E^3} \right)_{E=\mu} + \cdots
\end{aligned}
\tag{4.84}
$$

This expression is known as the **Sommerfeld formula**.

Heat Capacity of a Fermi Gas

The number of particles

$$
\begin{aligned}
N &= \int_{0}^{\infty} g(E) f(E) \mathrm{d}E = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_{0}^{\infty} E^{\frac{1}{2}} f(E) \mathrm{d}E \\
&= \frac{g_s V}{6\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \mu^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]
\end{aligned}
\tag{4.85}
$$

hence

$$
\mu = E_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]^{-\frac{2}{3}} = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \cdots \right] \tag{4.86}
$$

The energy

$$U = \int_0^\infty E g(E) f(E) \mathrm{d}E = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty E^{\frac{3}{2}} f(E) \mathrm{d}E$$

$$= \frac{g_s V}{10\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \mu^{\frac{5}{2}} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]$$

$$= \frac{g_s V}{10\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \mu^{\frac{3}{2}} E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \cdots \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]$$

$$= \frac{g_s V}{10\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \mu^{\frac{3}{2}} E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \cdots \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{E_F} \right)^2 + \cdots \right]$$

(4.87)

Our real interest is in the heat capacity. However, with fixed particle number N, the chemical potential also varies with temperature at quadratic order. We can solve this problem by dividing by Eq.(4.85) to get

$$\frac{U}{N} = \frac{3}{5} E_F \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \cdots \right] \tag{4.88}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} = N k_B \frac{\pi^2}{2} \frac{T}{T_F} \tag{4.89}$$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{g_s} \frac{N}{V} \right)^{\frac{2}{3}} \tag{4.90}$$

5 Relativistic Gases

$$E^2 = p^2 c^2 + m^2 c^4 \tag{5.1}$$

where m is now taken to be the **rest mass**.

- Non-relativistic case: $p^2 \ll m^2 c^2$

$$E = mc^2 \left(1 + \frac{p^2}{m^2 c^2} \right)^{\frac{1}{2}} = mc^2 \left(1 + \frac{1}{2} \frac{p^2}{m^2 c^2} \right) = \frac{p^2}{2m} + mc^2 \tag{5.2}$$

- Ultrarelativistic case: $p^2 \gg m^2 c^2$

$$E = pc = \hbar k c \tag{5.3}$$

5.1 The ultrarelativistic gas

Using the ultrarelativistic limit $E = pc = \hbar k c$, we can write the single-partition function

$$Z_1 = \int_0^\infty e^{-\beta \hbar k c} g(k) \mathrm{d}k \tag{5.4}$$

where

$$g(k)\mathrm{d}k = \frac{V k^2 \mathrm{d}k}{2\pi^2} \tag{5.5}$$

using the substitution $x = \beta \hbar k c$, we have

$$Z_1 = \frac{V}{2\pi^2} \left(\frac{1}{\beta \hbar c} \right)^3 \int_0^\infty e^{-x} x^2 \mathrm{d}x = \frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \propto V T^3 \tag{5.6}$$

We can also write Eq.(5.6) in a familiar form

$$Z_1 = \frac{V}{\Lambda^3} \tag{5.7}$$

where

$$\Lambda = \frac{\hbar c \pi^{\frac{2}{3}}}{k_B T} \tag{5.8}$$

The N-particle partition function Z_N is given by

$$Z_N = \frac{Z_1^N}{N!} \tag{5.9}$$

and hence

$$\ln Z_N = N \ln V + 3N \ln T + \text{constants} \tag{5.10}$$

or

$$\ln Z_N = N \ln V - 3N \ln \Lambda - N \ln N + N = N \ln \left(\frac{1}{n\Lambda^3} \right) + N \tag{5.11}$$

So we can derive U, C_V, F, p, S, H and G for an ultrarelativistic gas of indistinguishable particles.

- The internal energy U

$$U = -\frac{\mathrm{d}\ln Z_N}{\mathrm{d}\beta} = 3Nk_BT \tag{5.12}$$

- The heat capacity C_V

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B \tag{5.13}$$

- The Helmholtz function F

$$F = -k_BT\ln Z_N = -Nk_BT\ln V - 3Nk_BT\ln T + \text{constants} \tag{5.14}$$

$$F = -k_BT\ln Z_N = Nk_BT\left[\ln\left(n\Lambda^3\right) - 1\right] \tag{5.15}$$

- Pressure p

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} = nk_BT = \frac{u}{3} \tag{5.16}$$

- The enthalpy H

$$H = U + pV = 4Nk_BT \tag{5.17}$$

- Entropy S

$$S = \frac{U - F}{T} = Nk_B\left[4 - \ln\left(n\Lambda^3\right)\right] \tag{5.18}$$

- The Gibbs function G

$$G = H - TS = Nk_BT\ln\left(n\Lambda^3\right) \tag{5.19}$$

5.1.1   Adiabatic Expansion of an Ultrarelativistic Gas

The entropy S stays constant in the adiavatic expansion, which implies that

$$VT^3 = \text{constant} \tag{5.20}$$

or equivalently (using $pV \propto T$)

$$pV^{\frac{4}{3}} = \text{constant} \tag{5.21}$$

5.1.2 The Difference Between Non-relativistic Gas and Ultrarelativistic Gas

Property	Non-relativistic	Ultrarelativistic
Z_1	$\frac{V}{\lambda_{\text{th}}^3}$	$\frac{V}{\Lambda^3}$
	$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}}$	$\Lambda = \frac{\hbar c \pi^{\frac{2}{3}}}{k_B T}$
U	$\frac{3}{2} N k_B T$	$3 N k_B T$
H	$\frac{5}{2} N k_B T$	$4 N k_B T$
p	$n k_B T = \frac{2}{3} u$	$n k_B T = \frac{1}{3} u$
F	$N k_B T \left[\ln \left(n \lambda_{\text{th}}^3 \right) - 1 \right]$	$N k_B T \left[\ln \left(n \Lambda^3 \right) - 1 \right]$
S	$N k_B \left[\frac{5}{2} - \ln \left(n \lambda_{\text{th}}^3 \right) \right]$	$N k_B \left[4 - \ln \left(n \Lambda^3 \right) \right]$
G	$N k_B T \ln \left(n \lambda_{\text{th}}^3 \right)$	$N k_B T \ln \left(n \Lambda^3 \right)$
Adiabatic expansion	$V T^{\frac{3}{2}} = \text{constant}$	$V T^3 = \text{constant}$
	$p V^{\frac{5}{3}} = \text{constant}$	$p V^{\frac{4}{3}} = \text{constant}$

6 Phase Transitions

6.1 Liquid-Gas Transition

van der Waals equation of state

$$p = \frac{k_B T}{v - b} - \frac{a}{v^2} \tag{6.1}$$

$$\left(\frac{\partial p}{\partial v} \right)_T = -\frac{k_B T}{(v - b)^2} + \frac{2a}{v^3} = 0 \tag{6.2}$$

$$\left(\frac{\partial^2 p}{\partial v^2} \right)_T = \frac{2k_B T}{(v - b)^3} - \frac{6a}{v^4} = 0 \tag{6.3}$$

$$k_B T_c = \frac{8a}{27b} \tag{6.4}$$

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2} \tag{6.5}$$

6.1.1 The Clausius-Clapeyron Equation

We now want to find the equation that describes the phase boundary in the $p - T$ plane
   The requirement of chemical equilibrium

$$\mu_l = \mu_g \tag{6.6}$$

$$G(p, T, N) = \mu(p, T)N \tag{6.7}$$

and we have

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \tag{6.8}$$

hence

$$\mathrm{d}\mu = -\frac{S}{N}\mathrm{d}T + \frac{V}{N}\mathrm{d}p = -s\mathrm{d}T + v\mathrm{d}p \tag{6.9}$$

In the phase boundary we have $\mathrm{d}\mu_l = \mathrm{d}\mu + g$, so that

$$-s_l\mathrm{d}T + v_l\mathrm{d}p = -s_g\mathrm{d}T + v_g\mathrm{d}p \tag{6.10}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_g - s_l}{v_g - v_l} = \frac{l}{T(v_g - v_l)} = \frac{L}{T(V_g - V_l)} \tag{6.11}$$

we usually define the **latent heat**

$$L = T(S_g - S_l) \tag{6.12}$$

and also the **Clausius-Clapeyron equation**

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{T(v_g - v_l)} = \frac{L}{T(V_g - V_l)} \tag{6.13}$$

Now we estimate for the entropy discoutinuity at a vapour-liquid transition.

$$\frac{\Omega_g}{\Omega_l} = \left(\frac{V_g}{V_l} \right)^{N_A} = \left(\frac{\rho_g}{\rho_l} \right)^{N_A} = (10^3)^{N_A} \tag{6.14}$$

$$\Delta S = \Delta(k_B \ln \Omega) = k_B T \ln\left(10^3\right)^{N_A} \approx 7R \tag{6.15}$$

so that

$$L \approx 7RT_b \tag{6.16}$$

This relation is known as **Trouton's rule**.

6.1.2 Stability and Metastability

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{1}{N}\left(\frac{\partial G}{\partial p}\right)_T = v \tag{6.17}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_p = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_p = -s \tag{6.18}$$

$$p = p_0 \exp\left(\frac{2\gamma V_l}{rRT}\right) \tag{6.19}$$

6.1.3 Classification of Phase Transition

The **order** of a phase transition os the order of the lowest differential of G (or μ) that shows a discontinuity at T_c.

- **First-order phase transition**: the entropy S and the volume V (the first differential of G) shows a discontinuity. The heat capacity C_V is a second differential of G and thus it shows a sharp spike, as dose the compressibility.

- **Second-order phase transition**

6.1.4 Critical Exponents

Critical exponents describe the behaviour of physical quantities near continuous phase transitions. We will focus attention on physics close to the critical point.

$$\bar{T} = \frac{T}{T_c} \qquad \bar{v} = \frac{v}{v_c} \qquad \bar{p} = \frac{p}{p_c} \tag{6.20}$$

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2} \tag{6.21}$$

How various quantities change as we approach the critical point.

- What happens to the difference in densities $v_g - v_l$ as we approach the critical point along the co-existence curve?

$$\bar{p} = \frac{8\bar{T}}{3\bar{v}_l - 1} - \frac{3}{\bar{v}_l^2} = \frac{8\bar{T}}{3\bar{v}_g - 1} - \frac{3}{\bar{v}_g^2} \tag{6.22}$$

If we solve this for $\bar{T}$, we have

$$\bar{T} = \frac{(3\bar{v}_l - 1)(3\bar{v}_g - 1)(\bar{v}_l + \bar{v}_g)}{8\bar{v}_l^2 \bar{v}_g^2} \tag{6.23}$$

$$\bar{v}_{\mathrm{g}} - \bar{v}_{\mathrm{l}} = \varepsilon$$

$$\bar{v}_{\mathrm{l}} = 1 - \frac{1}{2}\varepsilon \qquad \bar{v}_{\mathrm{g}} = 1 + \frac{1}{2}\varepsilon \tag{6.24}$$

$$\bar{T} \approx 1 - \frac{1}{16}(\bar{v}_{\mathrm{g}} - \bar{v}_{\mathrm{l}})^2 \tag{6.25}$$

$$\bar{v}_{\mathrm{g}} - \bar{v}_{\mathrm{l}} \sim (T_c - T)^{\frac{1}{2}} \tag{6.26}$$

- How does the volume change with pressure as we move along the critical isotherm.

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = 0 \tag{6.27}$$

$$p - p_c \sim (v - v_c)^3 \tag{6.28}$$

- Compressibility

$$\kappa = -\frac{1}{v}\frac{\partial v}{\partial p}\bigg|_T \tag{6.29}$$

$$\left(\frac{\partial p}{\partial v}\right)_{T, v=v_c} = -a(T - T_c) + \cdots \tag{6.30}$$

$$\kappa \sim (T - T_c)^{-1} \tag{6.31}$$

Gibbs phase rule

$$F = C - P + 2 \tag{6.32}$$

6.1.5 Fluctuations

$$\langle N \rangle = V \frac{\partial p}{\partial \mu}\bigg|_{T,V} \tag{6.33}$$

6.2 The Ising Model

The Ising model consists of N sites in a d-dimensional lattice. On each lattice site lives a quantum spin that can sit in one of two states: spin up or spin down. We'll call the eigenvalue of the spin on the ith lattice site s_i. If the spin is up, $s_i = +1$; if the spin is down, $s_i = -1$.

$$E = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_i s_i \tag{6.34}$$

The notation $\langle ij \rangle$ means that we sum over all "nearest neighbour" pairs in the lattice and q means the number of nearest neighbours.

If $J > 0$, neighbouring spins prefer to be aligned ($\uparrow\uparrow$ or $\downarrow\downarrow$). In the context of magnetism, such a system is called a **ferromagnet**. If $J < 0$, the spins want to anti- align ($\uparrow\downarrow$). This is an **anti-ferromagnet**. We'll choose $J > 0$ in the following discussion although the difference are minor.

We work in the canonical ensemble and the partition function

$$Z = \sum_{\{s_i\}} e^{-\beta E} = \sum_{\{s_i\}} \exp\left(\beta J \sum_{\langle ij \rangle} s_i s_j + \beta B \sum_i s_i\right) \tag{6.35}$$

Our interest is in the average spin, or average **magnetization**

$$m = \frac{1}{N} \sum_i \langle s_i \rangle = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial B} \tag{6.36}$$

6.2.1 Mean Field Theory

$$
\begin{aligned}
s_i s_j &= [(s_i - m) + m][(s_j - m) + m] \\
&= (s_i - m)(s_j - m) + m(s_j - m) + m(s_i - m) + m^2 \\
&\approx m(s_i + s_j) - m^2
\end{aligned} \tag{6.37}
$$

The mean field approximation means that we assume that the fluctuations of spins away from the average are small which allows us to neglect the first term $(s_i - m)(s_j - m)$.

$$
\begin{aligned}
E_{\text{mf}} &= -J \sum_{\langle ij \rangle} \left[m(s_i + s_j) - m^2 \right] - B \sum_i s_i \\
&= \frac{1}{2} JNqm^2 - (Jqm + B) \sum_i s_i
\end{aligned} \tag{6.38}
$$

The effective magnetic field

$$B_{\text{eff}} = B + Jqm \tag{6.39}$$

Rewrite the partition function

$$Z = \sum_{\{s_i\}} e^{-\beta E} = e^{-\frac{1}{2}\beta JNqm^2} \left(e^{-\beta B_{\text{eff}}} + e^{\beta B_{\text{eff}}} \right)^N = e^{-\frac{1}{2}\beta JNqm^2} 2^N \cosh^N(\beta B_{\text{eff}}) \tag{6.40}$$

and the magnetization

$$m = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial B} = \tanh(\beta B + \beta Jqm) \tag{6.41}$$

We now can solve this equation to find the magnetization $m = m(T, B)$.

B = 0

-

$$k_B T_c = Jq \tag{6.42}$$

B ≠ 0

6.2.2 Critical Exponents

Consider the magnetization at $B = 0$.

$$m = \tanh(\beta Jqm) \approx \beta Jqm - \frac{1}{3}(\beta Jqm)^3 + \cdots \tag{6.43}$$

magnetic susceptibility χ

6.2.3 Some Exact Results for the Ising Model

As we mentioned above, there is an exact solution for the Ising model in $d = 1$ dimension and, when $B = 0$, in $d = 2$ dimensions.

6.2.4　1d Ising Model

$$E = -J \sum_{i=1}^{N} s_i s_{i+1} - \frac{B}{2} \sum_{i=1}^{N} (s_i + s_{i+1}) \tag{6.44}$$

The partition function

$$Z = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{i=1}^{N} \exp\left[\beta J s_i s_{i+1} + \frac{\beta B}{2}(s_i + s_{s+1})\right] \tag{6.45}$$

$$\langle s_i | T | s_i \rangle = \exp\left[\beta J s_i s_{i+1} + \frac{\beta B}{2}(s_i + s_{s+1})\right] \tag{6.46}$$

$$T = \begin{pmatrix} e^{\beta J + \beta B} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta B} \end{pmatrix} \tag{6.47}$$

$$Z = \mathrm{Tr}(\langle s_1 | T | s_2 \rangle \langle s_2 | T | s_3 \rangle \cdots \langle s_N | T | s_1 \rangle) = \mathrm{Tr}(T^N) = \sum_i \lambda_i^N \tag{6.48}$$

$$\sum_{s_N} \exp(\beta J s_{N-1} s_N) = e^{\beta J} + e^{-\beta J} = 2 \cosh \beta J \tag{6.49}$$

$$\begin{aligned} \lambda_\pm &= e^{\beta J} \cosh(\beta B) \pm \sqrt{e^{2\beta J} \cosh^2(\beta B) - 2\sinh(2\beta J)} \\ &= e^{\beta J} \cosh(\beta B) \pm \sqrt{e^{2\beta J}\left[1 + \sinh^2(\beta B)\right] - (e^{2\beta J} - e^{-2\beta J})} \end{aligned} \tag{6.50}$$

Let $B = 0$, then we have $\lambda_\pm = e^{\beta J} \pm e^{-\beta J}$, hence

$$Z = \lambda_+^N + \lambda_-^N = 2^N \cosh^N(\beta J) + 2^N \sinh^N(\beta J) \tag{6.51}$$

6.2.5　2d Ising Model

We will work on a square lattice and set $B = 0$.

6.3　Landau Theory

The Landau theory of phase transitions is based around the free energy.

$$F = -\frac{1}{\beta} \ln Z = \frac{1}{2} J N q m^2 - \frac{N}{\beta} \ln\left(2 \cosh \beta B_{\text{eff}}\right) \tag{6.52}$$

The equation above can be thought of as an expression for F as a function of m. The equilibrium is guaranteed if we sit at the minimum of F.

$$\frac{\partial F}{\partial m} = 0 \qquad \Rightarrow \qquad m = \tanh \beta B_{\text{eff}} \tag{6.53}$$

In the context of Landau theory, m is called an **order parameter**.

6.3.1 Second Order Phase Transitions

We consider a general system and denote the order parameter as m.

$$F(T, m) = F_0(T) + a(T)m^2 + b(T)m^4 + \cdots \tag{6.54}$$

We assume that $b(T) > 0$ for all T.

$$\frac{\partial F}{\partial m} = 0 \tag{6.55}$$

- When $a(T) > 0$, we have just a single equilibrium solution to Eq.(6.55) at $m = 0$.

- When $a(T) < 0$, we have two stable solutions

$$m = \pm\sqrt{\frac{-a}{2b}} \qquad T < T_c \tag{6.56}$$

If $a(T)$ is a smooth function then the equilibrium value of m changes continuously from $m = 0$ when $a(T) > 0$ to $m \neq 0$ at $a(T) < 0$. This describes a second order phase transition occurring at T_c, defined by $a(T_c) = 0$.

$$F(T) = \begin{cases} F_0(T) & T > T_c \\ F_0(T) - \frac{a^2}{4b} & T < T_c \end{cases} \tag{6.57}$$

Because $a(T_c) = 0$, the equilibrium free energy $F(T)$ is continuous at $T = T_c$. Moreover, the entropy S is also continuous at $T = T_c$

$$S = -\frac{\partial F}{\partial T} \tag{6.58}$$

$$C = T\frac{\partial S}{\partial T} \tag{6.59}$$

We assume that near $T = T_c$, we can write

$$b(T) \approx b_0 \qquad a(T) \approx a_0(T - T_c) \tag{6.60}$$

then we have

$$m_0 \approx \pm\sqrt{\frac{a_0}{2b_0}}(T_c - T)^{\frac{1}{2}} \qquad T < T_c \tag{6.61}$$

$$F_{\text{Ising}}(T, m) = -Nk_BT \ln 2 + \frac{NJq}{2}(1 - Jq\beta)m^2 + \left(\frac{N\beta^3 J^4 q^4}{24}\right)m^4 \tag{6.62}$$

6.3.2 First Order Phase Transitions

$$F(T, m) = F_0(T) + \alpha(T)m + a(T)m^2 + \gamma(T)m^3 + b(T)m^4 + \cdots \tag{6.63}$$

$$F_{\text{Ising}}(T, m) = -Nk_BT \ln 2 + \frac{JNq}{2}m^2 - \frac{N}{2k_BT}(B + Jqm)^2 + \frac{N}{24(k_BT)^3}(B + Jqm)^4 + \cdots \tag{6.64}$$